# Molecular Motion of Amorphous Silicone Polymers

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ABSTRACT: In this paper, we have studied silicone polymers based on poly(dimethylsiloxane) (PDMS) molecules, which have versatile applications in many fields because of their flexible molecular properties. These polymers are of interest because when used for high-voltage insulation, surfaces exposed to weather need to be hydrophobic because a hydrophilic surface can cause leakage currents. Indeed, after damaging electrical discharges, self-recovery of the hydrophobic surface occurs, requiring molecular diffusion and surface reconstruction for repair. We use large-scale, all-atom molecular dynamics simulations that enable an atomic-level description of molecular motion in mixed, amorphous, PDMS-based materials. The local properties that contribute to enhanced molecular motion are characterized based on their local structural and electrostatic environment. With this knowledge, molecular components with desirable diffusion properties may be designed for improved material functionality.
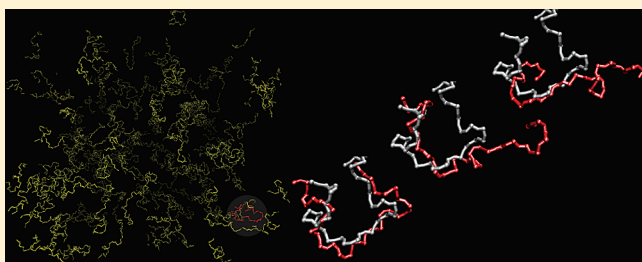
■ INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is a ubiquitous silicone polymer used for a wide range of technical and consumer applications. On the basis of the degree of polymerization (polymer length), functional groups, and the mixture ratios, the materials properties of PDMS vary greatly. For example, the mechanical and functionalization properties of PDMS are of interest for sensor applications[1] and biomedical devices,[2] whereas its rheological properties are important when insulation and rigidity are requirements.[3] Crosslinked PDMS-based polymers, in which individual molecules are chemically bonded, can exhibit lower surface tension. For applications in microfluidics and soft lithography, the surface hydrophobicity of PDMS may lead to the formation of air bubbles, deteriorating the fluid properties.[4,5]

A significant application of crosslinked PDMS-based devices is as insulators for high-voltage cables. For this application, insulating PDMS materials must have a hydrophobic surface. Decreased surface hydrophobicity due to surface oxidation is often caused by an electrical discharge.[6] Because the surface is exposed to weather fluctuations, the hydrophilic surface causes water and other molecules to accumulate, which can affect the important dielectric properties of the material. Occurring more frequently in highly crosslinked polymers and likely due to the oxidation of the C—C bond found at crosslinking sites,[7,8] leakage currents appear in those high-voltage insulators with reduced surface hydrophobicity.[7-10] Hydrophobic self-recovery eventually repairs the hydrophilic surface, a result that was quantified by mapping the UV/ozone-treated PDMS surface.[11] One recovery mechanism involves the diffusion of smaller molecules and may lead to dielectric recovery.[9,12] The other route for surface recovery is the structural rearrangement of dipoles on the surface.[10] Overall, the

self-diffusive properties of molecules lead to the return of desired insulation properties of rigid and crosslinked PDMS polymers used for high-voltage insulators. Improved materials may be designed by exploiting specific molecular properties suggested by simulation results of molecular self-diffusion with an atomic-level description.

The structure, dynamics, and self-diffusion properties of an amorphous, binary mixture of large PDMS and small poly(methylhydrosiloxane) (PMHS) were characterized with atomic-level molecular dynamics simulations. Molar masses and mixing properties were chosen to be similar to the precursor of a crosslinked and widely used silicone system commercially known as Sylgard-184 (Dow Corning) and other routinely used polymer blends.[13] The simulated system consisted of 100 vinyl-terminated PDMS molecules with a large degree of polymerization (DP = 978, ~72 500 g/mol) and 200 much smaller crosslinker PMHS molecules (DP = 32, ~1960 g/mol), for a total of more than 1 000 000 atoms (see Table 1 for a detailed comparison of the molecular types).
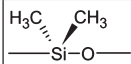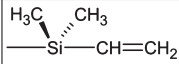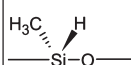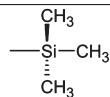
Understanding the local molecular motion is critical for explaining the diffusion of molecules, which in turn is an important property for understanding the dielectric recovery. Bulk properties derived from molecular simulations, such as diffusion coefficients, lack anomalous spatial and temporal effects for individual molecules and are potentially dependent on the duration of the simulation. Using all-atom, classical molecular dynamics, we investigated the effect of the environment, both

Table 1. Chemical Properties of the Molecular Components of the Amorphous System Poly(dimethylsiloxane) (PDMS) and Poly(methylhydrosiloxane) (PMHS)

	Backbone	Monomers (N)	Termination	# Molecules	Molar Mass	% Mass
PDMS	H_3C CH_3 —Si—O—	976	H_3C CH_3 —Si—CH=CH$_2$	100	72562.3 g/mol	95.0%
PMHS	H_3C H —Si—O—	30	CH_3 —Si—CH$_3$ CH_3	200	1966.2 g/mol	5.0%

structural and electrostatic, on the local periods of molecular motion. The origin of fast molecular motion was studied as a function of temperature, and fast-moving crosslinker molecules were analyzed to explain their faster diffusion. Simulation results provided an atomic-level description for the molecular motion and an understanding of the local structure that contributes to molecular self-diffusion. The interactions due to local electrostatics and the local packing around a molecule were two critical factors that together determine local molecular motion. Future polymer blends with desirable diffusion properties and faster self-recovery of surface hydrophobicity may be designed using computational methods.

■ METHODS

Molecular System. All simulation data were obtained from an amorphous system that consisted of two silicone polymer components. The first molecule, of which 100 were used, was a long PDMS chain with a degree of polymerization (DP) of 978. Both termini of every PDMS molecule consisted of vinyl groups, intended to be eventually reactive with the crosslinker backbone. The second molecule, of which 200 were used, was a shorter crosslinker molecule, namely, PMHS with DP = 32. In the latter, the reactive site for crosslinking was found on the 30 nonterminal Si atoms and consisted of a randomly oriented hydrogen instead of the methyl group found on PDMS. Terminal Si atoms on each crosslinker molecule were terminated with three methyl groups. The molecular properties are described in condensed form in Table 1. A cubic simulation cell of $(23.35 \text{ nm})^3$ is shown in Figure 1, with individual PDMS and crosslinker molecules highlighted for visual size comparison. The density of the simulation cell corresponded to a realistic density for this material at room temperature, namely, $\sim$0.99 g/cm^3. The total number of atoms was 1 026 300.

Force Field. An all-atom classical force field was used in order to characterize and explain atomic-level molecular movement and was implemented with LAMMPS code[14,15] on the IBM Blue Gene architecture.[16] Coarse-graining of atomic groups into larger pseudoatoms was not an option because the atomic resolution of the local electrostatic structure, specifically the reorientation of dipoles, would be lost. A polarizable force field would be more desirable, but for an amorphous system of this size, it would be too expensive computationally. The implemented force field was parametrized for PDMS and based on quantum chemistry calculations detailed by Smith et al.[17] Bonded energies were considered with either Class II[18,19] or harmonic terms. A custom Class II potential was created for the energetic discontinuity at the linearization point of the anharmonic Si—O—Si bond, using previously described methodology.[6,17] Nonbonded Lennard-Jones

interactions were characterized with a $1/r^6 + 1/r^{12}$ potential, which we fit to the Buckingham potential previously used for PDMS systems.[17] Nonbonded Coulombic interactions were treated with the standard $1/r$ interaction. Both Lennard-Jones and Coulomb pairwise energies were cut off at 10.0 Å and were not computed for 1−2 and 1−3 atom pairs, and they were scaled by 0.5 for 1−4 atom pairs. The SHAKE algorithm[20] was used for all covalent bonds involving H.

Partial atomic charges based on ref 17 were used. To describe different molecular structures, these charges were slightly modified to include different terminal groups, in particular, the terminal vinyl groups on each PDMS molecule and the Si—H bonds on each crosslinker molecule. On the PDMS molecules, partial charges on the vinyl carbons were −0.205 e. On the crosslinker molecules, the nonterminal Si atoms had a partial atomic charge of +0.804 e, and the H atoms bonded to those Si had a charge of −0.198 e. The total charge of each molecule was neutral, as was the entire system, with the exception of simulations that included a single negatively charged crosslinker.

Generating an Amorphous System. Generating an accurate amorphous system with a finite simulation cell is a challenging task that requires either impossibly long simulation times or creative methods for mixing.[21] To ensure proper liquid-like mixing and to decrease the simulation time necessary, we have softened the nonbonded potential terms. First, the repulsive and attractive nonbonded interactions were turned off so that molecules were able to pass through each other. Then, a small repulsive term was added to the pairwise interaction, which caused any overlapped atoms to experience weak repulsive forces that pushed them slightly apart. Throughout this process, the time step and cutoff were manipulated to prevent discontinuous integration and excessively large neighboring lists, respectively. Finally, the full attractive and repulsive nonbonded interactions were included, and full equilibration was allowed for more than 10 ns, resulting in realistic amorphous structures. Successful and sufficient mixing was achieved and confirmed by convergence of the radial distribution functions to glass-like structures.

Chemical Crosslinking via Simulation. With the help of a platinum catalyst, a crosslinking reaction occurs between the larger and smaller molecular components of the system. Crosslinking increases the average degree of polymerization and stiffens the material. The chemical reaction covalently bonds the vinyl group at the termini of each PDMS molecule to the Si—H backbone on the smaller crosslinker molecule (see Table 1). In our simulations, we have considered various crosslinking densities; the maximum was 50%. For this case, 100 of the 200 terminal vinyl groups were incrementally bonded to a crosslinker molecule. The end result was that many crosslinker molecules were bonded
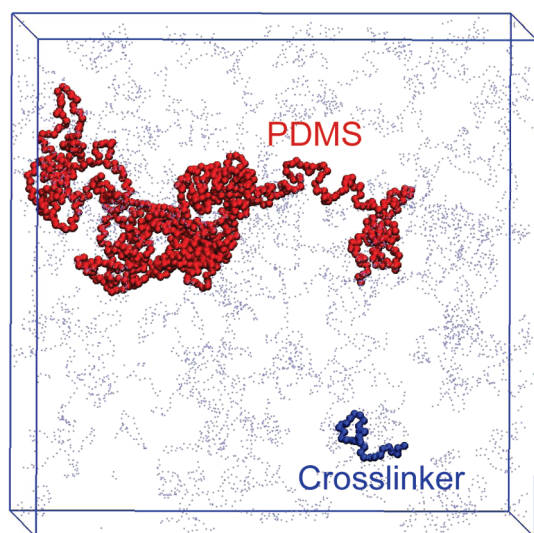
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Figure 1. Structural image of the simulation cell with a cubic length of 23.3 nm. One PDMS molecule and one crosslinker are highlighted to contrast the size of the molecules.

to more than one PDMS molecule, thus doubling the degree of polymerization for those PDMS molecules and reducing the number of free crosslinker molecules in the system. The overall diffusion is considerably attenuated for two reasons; first, there were many chains with a much larger degree of polymerization, and second, there were fewer free crosslinkers. Because the material became even more rigid after crosslinking and because there were fewer free crosslinking molecules for diffusion, we have analyzed molecular diffusion for the precursor system, before any crosslinking and where all of the molecules were free.

■ RESULTS

The self-recovery of a hydrophobic surface is an essential characteristic for PDMS-based materials used for high-voltage insulators. In these systems, electrical discharges can damage the chemical composition and the molecular structure of the polymer, thus rendering the surface hydrophilic and destroying the required dielectric properties. Self-recovery to a hydrophobic surface is based on molecular diffusion and surface rearrangement of molecules, specifically of charged or polar groups. The diffusion of molecules depends on their size and structure as much as on the surrounding matrix, and for this reason, we investigated the importance of the local structural and electrostatic environment for fast molecular motion.

Mean-Squared Displacements Showing Dependence on Temperature and Molecular Size. Using the amorphous polymer mixture, equilibration and production trajectories at four temperatures (T = 300, 500, 750, and 1000 K) were calculated with the canonical ensemble (NVT) with an integration time step of 0.5 fs and a Langevin thermostat (dampening every 10.0 ps). The total simulation times for each temperature, and after adequate equilibration, are shown in Figure 2.

Individual crosslinker molecules exhibited a wide range of MSDs at higher temperatures, as compared to the much larger PDMS molecules (see Figure 2 top, inset). This indicates that the molecular movement of the smaller molecules greatly varied between molecules. For 300 and 500 K, both the PDMS (Figure 2, bottom) and the crosslinker molecules (Figure 2, top) have
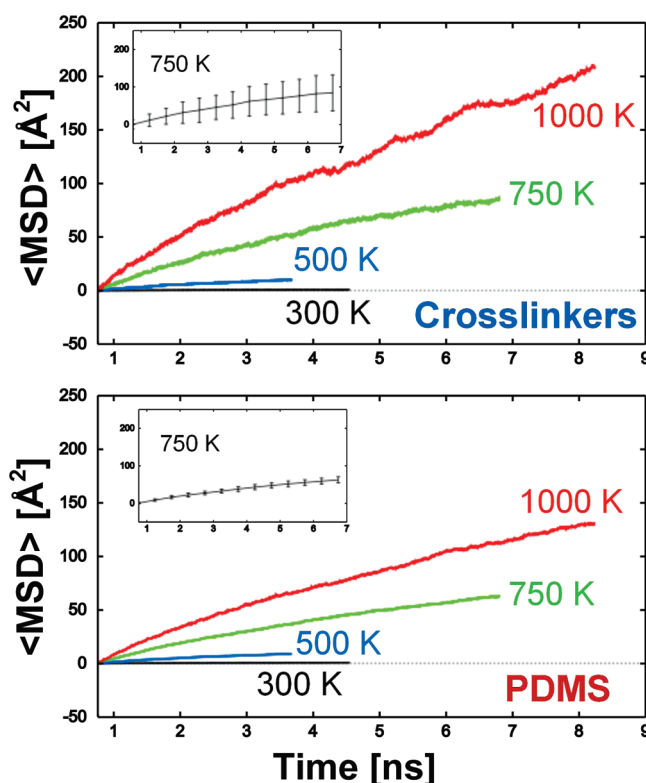

Figure 2. Mean-squared displacements (MSD) averaged over the set of 200 crosslinker molecules (top panel) and 100 PDMS molecules (bottom panel), with correction for the motion of the center of mass. All data are shown after significant equilibration but centered at the origin for comparison. The temperature effect was more pronounced for 750 and 1000 K, where the crosslinker molecules, on average, moved much more than PDMS. Indeed, the crosslinker MSD shows a large standard deviation (top, inset) as compared to PDMS (bottom, inset), indicating a wide distribution of displacement for crosslinker molecules at 750 K. This large spread is triggered by short periods of fast molecular motion due to local structural and electrostatic factors.

approximately the same MSD (relative to the center of mass of the system). For 750 and 1000 K, the molecular MSD rises sharply, with some crosslinker molecules moving much faster than PDMS. The glass transition temperature for this system was between 500 and 750 K, and therefore, we focus on results from 750 K, where there is enough diffusion of crosslinker molecules for the trajectory lengths that we have simulated but there is not too high of a temperature to create unrealizable physical conditions.

The diffusion coefficient (D) for a trajectory is calculated from the squared spatial deviation from the initial, equilibrated state, called the MSD

$$\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 6Dt \tag{1}$$

where t is the simulation time.[22] The Arrhenius plot reveals a linear behavior for diffusion coefficients (D), indicating a single-rate, thermally activated process (see Figure 3). The activation energy for the glass transition of the combined system is 114.3 J/mol. When the overall diffusion is compared for different temperatures, the spread of the diffusion coefficients for crosslinker molecules is considerably larger at high temperatures (T = 750, 1000 K) than that at low temperatures. At these higher temperatures, and depending on the local environment, some crosslinker
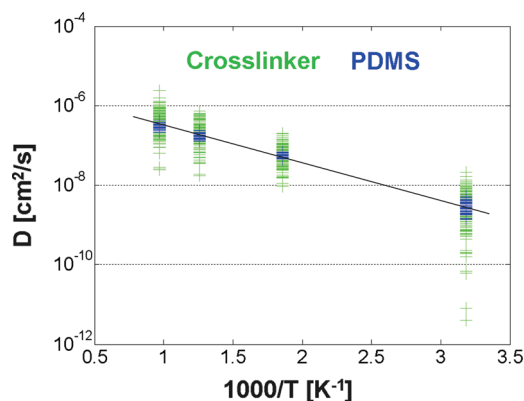
Figure 3. Diffusion coefficients (D) for individual molecules, calculated from individual MSDs, are shown as an Arrhenius plot. The linear slope for the combined PDMS and crosslinker system indicates a single rate-limited, thermally activated process. Crosslinker diffusion coefficients (green crosses) exhibit a very large spread at $T = 750$ and 1000 K, meaning that some move at a rate similar to that of PDMS, whereas others move at a much faster rate.
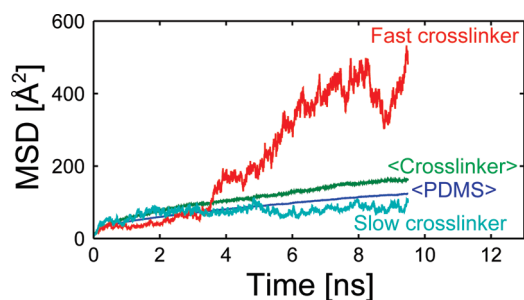

Figure 4. MSDs of representative "fast" and "slow" crosslinker molecules are shown relative to the averaged crosslinker and PDMS. Crosslinker molecules sometimes move faster than the molecular mean due to short bursts (<500 ps) of fast motion.

molecules are less constrained and have enhanced molecular motion.

Figure 4 shows the mean MSD for PDMS and crosslinker molecules, as well as that for a representative "fast" and "slow" crosslinker molecule. Some slow crosslinker molecules had a MSD comparable to that of the much slower PDMS molecules, or even smaller. Still, other fast crosslinkers had a large MSD, which was attributed to several short periods of fast molecular motion (<500 ps). It is these interesting bursts of fast motion that we have investigated.

Local Motion Depending on the Structural and Electrostatic Environment. Periods of fast motion for crosslinker molecules contribute to an enhanced MSD and to improved self-diffusion of certain crosslinker molecules. One representative crosslinker molecule is shown in Figure 5 (top) with the periods of fast motion highlighted. First, in periods of fast motion of a crosslinker molecule, the Coulombic interactions between that molecule and its local environment are regularly attractive (Figure 5, center). The net Coulombic potential energy (E_{Coul}) experienced by a crosslinker molecule shows that electrostatic interactions determine periods of fast motion. In addition to the attractive electrostatic environment, a reduced local density allows the molecule to move more freely. Radial distribution functions are helpful to characterize the "density" of the local environment
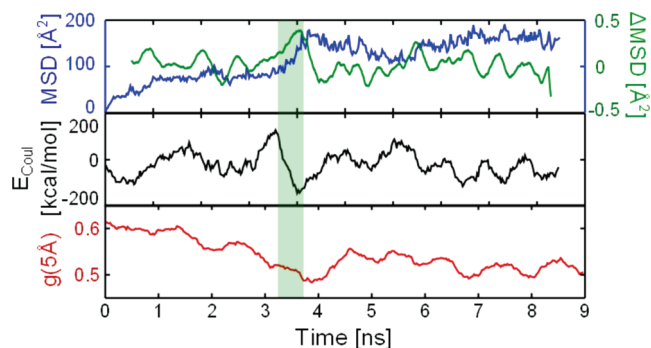

Figure 5. MSD, change in MSD (ΔMSD), Coulomb electrostatic interaction (E_{Coul}) between a molecule and its environment, and the radial distribution function at 5 Å ($g(5.0$ Å)) for a representative molecule. Fast molecular motion (top) is correlated to periods of electrostatic (Coulomb) attraction (center) as well as fewer neighboring atoms (bottom).

around and excluding a single crosslinker molecule. We also count the number of atoms within a 5.0 Å thick shell around the target crosslinker molecule and use that number to provide a measure of the structural freedom that the molecule experiences (5 Å is a distance sufficiently large to capture the local environment but small enough not to lose local precision). The correlation between the periods of fast motion (Figure 5, top), the attractive electrostatic environment (Figure 5, center), and the reduced local density (Figure 5, bottom) indicates that both structural and electrostatic factors contribute to molecular motion and lead to enhanced self-diffusion of individual molecules.

Statistical Analysis of Fast Molecular Motion. Using the simulation data with $T = 750$ K, we performed additional analyses on the local environment for the set of crosslinker molecules. Over the entire trajectory, the mean E_{Coul} experienced by the crosslinker molecules is slightly positive, +10.3 kcal/mol. However, during periods of fast molecular motion, individual crosslinkers experience an average E_{Coul} of −31.9 kcal/mol. In the same periods, the change in the radial distribution function for fast molecules is always negative (on the order of −0.05 units, which is considerable). In addition to attractive Coulombic interactions for crosslinkers during periods of fast motion, the radial distribution function exhibits a decrease from the mean value for individual crosslinker molecules. Figure 6 shows a histogram for the ΔMSD, subtracted from the mean, for the time periods that have both the lowest 10% of E_{Coul} and the smallest 10% of the radial distrubtion function $g(5.0$ Å). The molecular motion is asymmetric and, in general, more positive, indicating that the periods of fastest diffusion depend on both an attractive electrostatic environment (E_{Coul}) and less packing, as indicated by the decreased radial distribution function.

Charged Test Molecules. To test the hypothesis that both the structural packing and nonbonded Coulombic interactions are important for driving fast molecular motion, a single crosslinker molecule was oxidized, and additional simulations were performed at $T = 750$ K. In this one molecule, one of the three terminal methyl groups was replaced with a carboxylate group ($-COO^-$), and a negative charge was distributed on the oxygen atoms so that the net charge of the termination group and the total molecule was −1.0 e. The overall diffusion for the charged crosslinker molecule, despite the charged group being on only one end of the molecule, was one of the highest among the other crosslinkers, suggesting that charged molecules will have
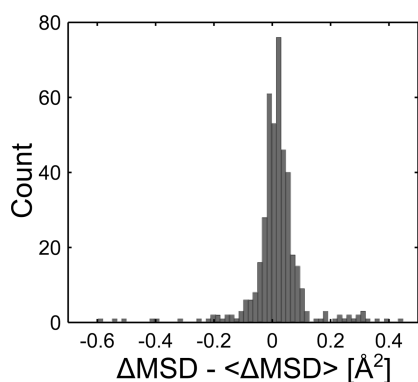
Figure 6. After grouping time periods that correspond to both the lowest 10% of E_{Coul} and the smallest 10% of the radial distribution functions ($g(5.0 \text{ Å})$) for individual crosslinker molecules, the ΔMSD for those periods, subtracted from the mean, is plotted as a histogram. There is considerably more "fast" diffusion for these periods, shown as positive ΔMSD.
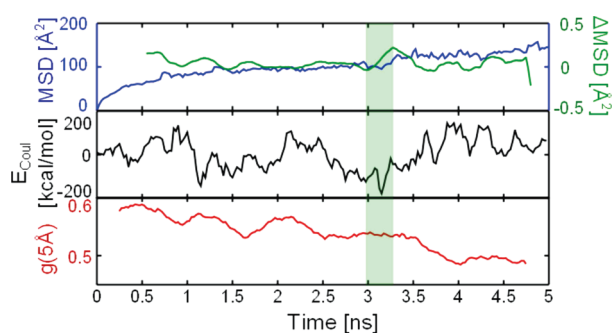

Figure 7. MSD, ΔMSD, and E_{Coul} between a molecule and its environment, and the radial distribution function at 5 Å ($g(5.0 \text{ Å})$) for a negatively charged crosslinker molecule. Fast molecular motion (top) is similarly correlated to periods of electrostatic Coulombic attraction (center) and fewer neighboring atoms (bottom).

enhanced diffusion. The MSD for the charged molecule is shown in Figure 7 (top), and periods of fast motion are highlighted. Similar to the neutral crosslinker molecules, this negatively charged molecule undergoes short periods of rapid molecular motion, which correspond to a negative (or neutral) Coulombic environment (Figure 7, center) as well as a decreased radial distribution function (Figure 7, bottom). Similar to results for the fast neutral crosslinker molecules, the charged molecule experiences short periods of attractive Coulombic forces in addition to reduced local density at these times when its molecular motion is fastest. Together, these contribute to short bursts of fast molecular motion which leads to enhanced self-diffusion.

DISCUSSION

Electrical discharges may damage PDMS-based materials used for high-voltage insulators. The chemical explanation is based on oxidation and charge formation on the surface, which decreases surface hydrophobicity and causes leakage currents. Eventually, self-recovery occurs, the molecular mechanism of which is based on the diffusion of smaller molecules to the surface. The molecular motion for PDMS-based amorphous mixtures is highly nonlinear and depends on the electrostatic and local structural environments. Small crosslinker molecules may undergo periods of rapid motion relative to the overall system dynamics. During

periods of fast motion, these crosslinker molecules experience an attractive electrostatic environment (Coulomb) and find themselves with fewer neighboring atoms, a state characterized by a decreased radial distribution function. Future polymer blends may be designed a priori to include polarized or hydrophobic charged groups to improve the diffusion properties of the polymers at the hydrophobic surface.

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